A NEW SEPARATION OF THORIUM

FROM

CERIUM, LANTHANUM AND DIDYMIUM

BY

METANITROBENZOIC ACID

AND ITS APPLICATION TO

THE DETERMINATION OF THORIUM IN MONAZITE

By

ARTHUR C. NEISH, A. M.

Dissertation
Submitted in Partial Fulfillment of the Requirements for the Degree of
Doctor of Philosophy in the Faculty of Pure Science of
Columbia University.

NEW YORK CITY
1904

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GEO. G. PECK
117 CHAMBERS ST.
NEW YORK

INTRODUCTION.

The work described in this thesis was undertaken with the object of finding a shorter and more satisfactory method for the determination of thorium in monazite sands.

The requirements of such a method are first, an accurate separation of thorium from cerium, lanthanum and didymium; second, rapidity and ease of manipulation; third, an inexpensive reagent and one which does not involve the use of alcohol.

It is believed that the method herein described meets these conditions.

As the analytical methods have been so recently reviewed by Metzger, J. Am. C. S. XXIV, 1902, 901, and a bibliography to the entire literature of thorium recently published by Joüet, Smithsonian Miscellaneous Collections No. 1374, the usual historical review of the literature pertaining to the subject is omitted.

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May 1, 1902.

ACKNOWLEDGEMENT.

This investigation was carried out under the direction of Professor Edmund H. Miller and I wish to gratefully acknowledge my most sincere thanks for his kind interest and advice.

A. C. N.

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A NEW SEPARATION OF THORIUM FROM CERIUM, LANTHANUM AND DIDYMIUM.

Preparation of Pure Thorium Nitrate.

The pure thorium nitrate was made by dissolving two hundred grams of "C. P" thorium nitrate, containing a small percent of cerium, in water in thirteen beakers each holding about 1000 c.c. To each beaker 150 c.c. of hydrogen peroxide Marchand's (Medicinal containing about 4% H_2O_2) was added (10 c.c. for every 0.5 gram ThO_2). The solutions were heated to 85° C. and allowed to settle. The precipitates were washed by decantation, and at the end of the sixth decantation the filtrate gave no test whatever for cerium on the addition of ammonia. The precipitates were transferred to a large Büchner funnel and the washing continued, stirring the precipitate with a spatula. The precipitate was transferred to a large evaporating dish, and 250 c.c. of concentrated nitric acid added, which readily dissolved the precipitate when a little heat was applied. The solution was evaporated to dryness, taken up with water diluted and divided among the thirteen beakers so that each contained about a litre, and the thorium reprecipitated as before. The precipitate was dissolved in nitric acid and evaporated to dryness, and dried in the air bath for three days at 115° C. This gave thorium nitrate of the highest purity containing no free nitric acid.

Sixty grams of this thorium nitrate was dissolved in seven litres of water, well shaken and divided among several well stoppered bottles.

Standardizing the Thorium Solution.

A very accurately standardized burette was used to measure out the thorium nitrate solution; it was connected to the bottle by glass tubing so as to facilitate filling without any chance of change due to evaporation or contamination.

Different amounts of thorium solution were run into a number of small beakers and heated to boiling, and a boiling solution of oxalic acid* was added a little at a time with constant stirring. After cooling the precipitate was filtered and washed with water. If precipitated from cold solutions the precipitate runs through the paper, but from hot solutions no trouble in filtering is encountered. The paper containing the thorium oxalate was placed in a weighed platinum crucible, gently heated with a Bunsen burner until dry and the paper charred, then the heat was increased and the oxalate changed to oxide; it was next heated by a blast lamp for fifteen minutes, cooled and weighed.

The following table gives the results:

C.C. $Th(NO_3)_4$	C.C. (COOH)	Weight ThO_2	ThO_2 in 1C.C.
25	20	.1128	.004512
25	20	.1128	.004512
50	40	.2256	.004512
50	40	.2255	.004510
50	40	.2255	.004510
50	40	.2255	.004510

Precipitants Tried.

Many organic precipitants were tried, mostly weak organic acids in the hope of finding one that would give a sharp separation, and a precipitate which would filter quickly without the use of alcohol.

The results are briefly as follows:

Gallic acid precipitates thorium quantitatively from a hot alcoholic solution as a flocculent slimy precipitate. Salts of cerium, lanthanum and didymium are not precipitated.

Tannic acid precipitates thorium quantitatively, but cerium, lanthanum and didymium are not precipitated.

Citric acid precipitates all from an acetone solution.

*Saturated in the cold.

Salicylic acid precipitates thorium. The precipitate is soluble in excess of the reagent.

Oleic acid in a strong alcoholic solution precipitates thorium and cerium. The cerium precipitate is soluble in excess, the thorium insoluble.

Linoleic acid precipitates all if insufficient alcohol is present, but with sufficient alcohol the cerium, lanthanum and didymium readily dissolve, the thorium is apparently insoluble.

Paratoluic acid gave a precipitate of thorium but none with cerium, lanthanum and didymium.

Oxy iso-phthalic acid gave a white curdy precipitate of thorium in an aqueous solution, almost quantitative, the other three earths gave no precipitate.

Benzoic acid precipitated thorium quantitatively from aqueous solution, the cerium, lanthanum and didymium were not precipitated. This method gives trouble on account of the very slight solubility of benzoic acid in water.

The three nitrobenzoic acids gave white precipitates with a neutral solution of thorium nitrate, while cerium, lanthanum and didymium gave no precipitate. The meta acid which is the most soluble in water precipitated the thorium quantitatively. This acid is the principal product of the nitration of benzoic acid, the yield being about 75%; but as the ortho and para acids as well as benzoic acid act similarly it is not necessary to use pure metanitrobenzoic acid, so that the reagent is one readily obtained.

Potassium iodate precipitates all four as heavy white precipitates.

Ammonium vanadate precipitates thorium, lathanum and didymium as canary yellow precipitates; the cerium precipitate has an orange color.

Lead acetate in a solution acid with nitric acid produces a white precipitate with thorium, which increases when heated but is incomplete. Cerium, lanthanum and didymium are not precipitated.

Arsenious oxide cream precipitates all four quantitatively in a solution containing sodium acetate.

Sodium tungstate precipitates all four as white precipitates.

Quantitative Precipitation of Thorium by Metanitrobenzoic Acid.

The solution of the precipitant is made by dissolving from three and a half to four grams of the acid in a litre of hot water (about 80° C), when all is in solution, it is allowed to stand over night when a slight amount will separate out as feathery crystals. The solution is filtered to free it from any crystals and foreign matter.

Thorium nitrate solution was run into a 300 c.c. beaker and a solution of the precipitant added very slowly with constant stirring; about 150 c.c. gave a liberal excess for 25 c.c. of thorium solution equivalent to .1128 grams of ThO_2. This produces a heavy white opalescence which soon collects on standing but rapidly on heating. The beaker was heated on the water bath to a temperature between 60°–80° C for fifteen minutes. The opalescence disappears and the bulky precipitate settles to the bottom in large flocks having much the appearance of silver chloride. The solution can either be filtered hot or allowed to cool, the precipitate is washed first by decantation and finally on the filter paper with a 5% solution of the precipitant. The precipitate and paper are not dried, for reasons given later, but placed moist in a weighed platinum crucible and carefully heated with the cover off, then after the paper and volatile matter driven off, heated with the full flame of a Bunsen burner until white, then covered and ignited for fifteen minutes in the blast lamp, cooled, and the thorium oxide weighed.

The following table shows that thorium is quantitatively precipitated from a neutral solution of the nitrate by metanitrobenzoic acid:

C.C. $Th(NO_3)_4$	C.C. Precipitant	ThO_2 found	ThO_2 taken	Error
50	300	.2256	.2256	+0000
25	150	.1132	.1128	+0004
36	150	.1630	.1625	+0005

Separation of Thorium from Cerium, Lanthanum and Didymium.

The next step was to try the separation of thorium from mixtures with cerium, lanthanum and didymium, and then from mixtures of thorium from all three.

As before, known volumes of thorium nitrate solution were placed in beakers, known quantities of cerium, lanthanum and didymium oxides were added in the form of nitrates, then an excess of metanitrobenzoic acid was added slowly with constant stirring, the solutions heated on the water bath, filtered and washed by decantation with a 5% solution of the precipitant. The moist precipitant and paper were placed in a weighed platinum crucible, heated and ignited, with the precautions given above, and the thorium oxide weighed.

A separatory funnel with a capacity of 75 c.c. was found very convenient, both as a measure of the volume added and for adding the solution slowly while stirring.

The test for cerium in the filtrate by ammonia and hydrogen peroxide is of no use as the metanitrobenzoic acid itself gives the same color.

The following results will show the efficiency of the separation:

C.C. $Th(NO_3)_4$	C.C. Precipitant	Total Volume	Weight CeO_2	Weight Di_2O_3	Weight La_2O_3	ThO_2 taken	ThO_2 found	Error
25	150	175	.1120			.1128	.1141	+0013
25	"	"		.1120		.1128	.1140	+0012
25	"	"			.1120	.1128	.1143	+0015
25	"	"	.1120	.1120	.1120	.1128	.1199	+0071
25	"	"	.1120	.1120	.1120	.1128	.1196	+0068
25	"	"	.0560	.0560	.0560	.1128	.1162	+0034

These experiments showed that one precipitation will not separate thorium from an equal weight of cerium, lanthanum or didymium, or from an equal or one half the amounts of all three. A nearly constant amount of each is carried down.

A reprecipitation being necessary many methods were tried to change the thorium metanitrobenzoate to thorium nitrate. The precipitate is readily soluble in nitric acid, but on evaporating this solution a hard, insoluble skin is left which incloses

the impurities, making the second precipitation useless. The precipitate was dissolved off the paper into the precipitation beaker with hot dilute nitric acid (1:5), the paper well washed with hot water, the solution in the beaker diluted to about 150 c.c. and twenty-five c.c. of metanitrobenzoic acid added. Then methyl orange was added until the solution became decidedly red, and then dilute ammonia (1:10) run in from a burette very slowly, with constant stirring until the solution turns from deep red to light red or pink. The clear solution after the addition of some ammonia becomes opalescent, due to the reprecipitation of thorium metanitrobenzoate, and as more is added the precipitate becomes white and flocculent increasing as more ammonia is added.

When the precipitate becomes flocculent the ammonia was added with great care, drop at a time, and the solution thoroughly stirred after every addition.

If the process of neutralization were carried to the yellow tint the other earths would precipitate.

The addition of ammonia is carried on until the red changes to pink; this marks the neutralization of the mineral acid and the weak acid metanitrobenzoic keeps the indicator pink. Very few drops more of ammonia would change the pink to yellow.

The solution of the precipitant changes methyl orange decidedly red only when considerable quantities are added, and then the same depth of color which mineral acids give is not produced. The 25 c.c. of metanitrobenzoic acid is sufficient to produce the pink.

At this point, the pink tint, all the thorium should be precipitated, but to ensure a complete precipitation 50 c.c. more of the precipitant is added, and the beaker heated on the water bath as before, filtered, washed with a 5% solution of the precipitant and either ignited and weighed or redissolved in nitric acid and the neutralization repeated.

The following table shows the results with three precipitations:

C.C.Th $(NO_3)_4$.	C.C. Precipitant.	Volume.	CeO_2.	Di_2O_3.	La_2O_3.	ThO_2 taken.	ThO_2 found.	Error.
25	150	175	.0560			.1128	.1129	+0001
25	"	"		.0560		.1128	.1131	+0003
25	"	"			.0560	1128	.1134	+0006
50	300	350	.0560	.0560	.0560	.2256	2263	+0008
26	150	175	.1120			.1173	.1179	+0006
25	"	"		.1120		.1128	1129	+0001
25	"	"	.1120	.1120	.1120	.1128	.1135	+0007

The above results being satisfactory the separation was tried on mixtures in the proportions usually found in monazite sands.

The next table shows the results with three precipitations:

C.C.Th $(NO_3)_4$.	C.C. Precipitant.	Volume.	CeO_2.	Di_2O_3.	La_2O_3.	ThO_2 taken.	ThO_2 found.	Error.
25	150	175	.5000	.3000	.2500	.1128	.1136	+0008
25	"	"	"	"	"	.1128	.1137	+0009
25	"	"	"	"	"	.1128	.1140	+0012
25	"	"	"	"	"	.1128	.1136	+0008
25	"	"	"	"	"	.1128	.1137	+0009
25	"	"	"	"	"	.1128	.1136	+0008
25	"	"	"	"	"	.1128	.1134	+0006

It was thought that with greater dilution a closer separation could be obtained with two precipitations.

The following series proves this to be the case:

C.C. $Th(NO_3)_4$	C.C. Precipitant	Volume	CeO_2	Di_2O_3	La_2O_3	ThO_2 taken	ThO_2 found	Error
25	150	700	.5000	.3000	.2500	.1128	.1126	—0002
25	"	700	"	"	"	.1128	.1126	—0002
25	"	700	"	"	"	.1128	.1125	—0003
25	"	900	"	"	"	.1128	.1132	+0004
25	"	700	"	"	"	.1128	.1123	—0005

The separation was next tried to see if one precipitation would separate thorium from cerium in the proportions they are present in Welsbach mantles. Nos. 3 and 4 were precipitated, giving slightly low results:

	C.C. $Th(NO_3)$	C.C. Precipitant	Volume	CeO_2	ThO_2 taken	ThO_2 found	Error
1	25	150	300	.0011	.1128	.1128	0000
2	25	150	"	.0011	.1128	.1128	0000
3	25	150	"	.0011	.1128	.1126	—0002
4	25	150	"	.0011	.1128	.1125	—0003

The Behavour of Other Elements.

Glucinum gave no precipitate, cold or hot.
Gadolinium " " "
Yttrium " " "
Titanium " " "
Samarium " " "

Zirconium gave a white opalescence and precipitate, which increased on heating.

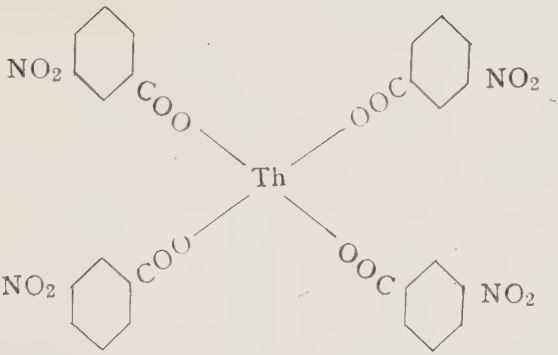
Erbium gave an immediate white curdy precipitate in the cold with little change on heating; the precipitation is quantitative.

The following commoner salts were tried, although none are apt to be present in the analysis of monazite: calcium chloride, barium chloride, magnesium chloride, potassium alummium sulphate, potassium chromium sulphate, ferrous sulphate, ferric sulphate, zinc sulphate, manganous sulphate, nickel nitrate, cobalt nitrate, bismuth nitrate, silver nitrate, lead nitrate, cadmium nitrate, copper nitrate, arsenious acid, arsenic acid, potassium antimonyl tartrate (tartar emetic), ammonium molybdate, auric chloride, platinum chloride, ammonium tungstate, uranium nitrate, mercurous nitrate, mercuric nitrate, stannous chloride and sodium stannate. With the exception of the last four they gave no precipitate. The precipitates with mercurous and mercuric nitrates were very heavy, white and curdy in the cold but dissolved on heating.

Composition of the Precipitate.

The precipitate used for the determination of its composition was made by dissolving the pure thorium nitrate in water in a large beaker and precipitated with an excess of metanitrobenzoic acid. The precipitate after heating on the water bath was washed by decantation then on the filter, a Büchner funnel, with a large amount of water to make the washing complete. The precipitate was transfered in a cake to a glass plate and dried for days in the air bath at 115° C. When thoroughly dried it was broken and pulverized and again dried for two days, being frequently stirred so as to ensure complete drying.

It was assumed that thorium would combine with four molecules of the acid as $Th(C_6H_4NO_2COO)_4$, written graphically.



The percentage composition calculated from this assumption gave:

Th=25 93%, C=37.46%, H=1.79%, N=6.26%, O=28.54.

The determination of carbon and hydrogen was made in a combustion furnace. The precipitate was placed in a weighed platinum boat with the hope that a determination of thorium could be made, but the precipitate burned so rapidly that some was invariably thrown out of the boat, and then it was almost impossible to collect it pure or completely; the trouble was partly remedied by placing a piece of platinum foil loosely on top of the boat, but even this did not give good results. Separate determinations for thorium by direct ignition were made.

The water was caught in a U tube containing pumice and sulphuric acid, the carbon dioxide in two U tubes, the first filled with soda-lime, the second having the first arm filled with soda-lime, the other with calcium chloride.

Weight of Precipitate.	%Th found.	%Th theory.	Error %.	%H found.	%H theory.	Error %.	%C found.	%C theory.	Error %.
.3312				1.85	1.79	+.06			
.2301	26.45	25.93	+.52	2.17	1.79	+.38	37.12	37.46	— .34
.3269				1.97	1.79	+.18	37.43	37.46	— .03
.1661	27.25	25.03	+1.32	2.29	1.79	+.50	37.48	37.46	+ .02
.5061	26.13	25.93	+.20	1.91	1.79	+.12	37.32	37.46	— .14
.7698				1.85	1.79	+.06	36.78	37.46	— .68

Determinations of thorium by direct ignition were made by carefully igniting the precipitate in a platinum crucible and blasting for fifteen minutes.

Weight of Precipitant.	Weight of ThO_2.	%Th found.	%Th theory.	Error %.
.3647	.1077	25.95	25.93	+.02
.5550	.1640	25.97	25.93	+.04
.3213	.0952	26.0	25.93	+.07
.6677	.1979	26.05	25.93	+.12

Determinations of nitrogen by the Dumas method were also made.

Weight of Precipitant.	%N found.	%N theory.	Error %.
.5067	6.42	6.26	+.16
.3130	6.48	6.26	+.22

These results uphold the formula assigned the precipitate formed by precipitating thorium by metanitrobenzoic acid.

Properties of Thorium Metanitrobenzoate.

The precipitate when dry presents very peculiar properties; it is snow white, very light and is electrified. When pressed or touched with a glass rod or a brush it acts like pith balls being first attracted, then repelled by the rod, so that it is impossible to handle it without loss, even the transfer of a precipitate to a platinum crucible cannot be done without loss; for this reason the wet precipitate is always ignited. The thorium metanitrobenzoate is radioactive, giving after an exposure of five days to an X Ray plate a faint image, while the thorium oxide produced from the ignition of the metanitrobenzoate, and the oxide separated from monazite sands by metanitrobenzoic acid gave about four times the effect.

When thorium metanitrobenzoate is ignited a large volume of gas is given off which burns with a sooty flame, leaving after complete ignition thorium oxide, snow white and in a very loose condition. This oxide when placed in a platinum boat inside a platinum combustion tube and strongly heated with two blast lamps, gave off white fumes similar to those obtained by Metzger* from the oxide obtained by the ignition of thorium fumarate. These fumes were collected in a small glass tube but disappeared after a few minutes.

Thorium metanitrobenzoate is insoluble in water, it is easily soluble in, and prevented from precipitation by hydrochloric, nitric, sulphuric, and acetic acids. Tartaric acid or tartrates dissolve the precipitate, from which solution the thorium cannot be precipitated either by ammonium hydroxide, potassium hydroxide or oxalic acid. Oxalic acid dissolves the precipitate with the formation of a white crystalline precipitate of thorium oxalate. Sodium carbonate dissolves the precipitate with the production of a flocculent precipitate soluble in excess of sodium carbonate. Potassium hydroxide decomposes it with the formation of thorium hydroxide. It is soluble in acetone; alcohol and ether have no solvent effect.

Monazite Analysis.

The practical application of the precipitation of thorium by metanitrobenzoic acid was applied to the analysis of monazite sands. The results were checked against the two shortest and best methods, the combination method, and the fumaric acid method of Metzger.† Five sands were analyzed three from Brazil and two from North Carolina.

Combination Method.

Two grams of the sand were ground to a fine powder and weighed out into a porcelain crucible (45 m.m.), about 10–15 c.c. of concentrated sulphuric acid added and stirred

*J. Am. C. S., xxiv, 1902, 901.
†J. Am. C. S., xiv, 1902, 901.

with a small glass rod, which is left in the crucible throughout the digestion. The crucible was placed on a hot plate, heated up gradually and stirred cautiously to allow the escape of bubbles of gas, which are only formed at first, and cause loss if the heating is not done carefully. The heat was increased, or the crucible moved to the hotter part of the plate until a constant cloud of sulphur trioxide was given off. When the excess of acid had evaporated more acid was added, the contents stirred with the glass rod and the digestion continued. As a rule the digestion lasted all day, since the solution of the sulphates in water was allowed to stand overnight, but two results are given where the digestion lasted only three hours so that longer digestion is unnecessary. At the end of the digestion the phosphates present in the monazite sand were all changed to sulphates, the crucible now contains about 10 c.c., this was well stirred and after cooling the crucible in ice water, the mass was allowed to drop from the rod, a drop at a time, with constant stirring into a beaker containing 600 c.c. of water cooled to 0°C. After all the liquid was added, the crucible itself was placed in the beaker, and the whole allowed to stand, best over night. If it is a refined sand and free from quartz the residue on the bottom of the beaker should be small, but if there is a flocculent precipitate it is apt to be hydrated sulphate of thorium. In this case the best thing to do is to start another portion, using greater care in adding the mass to the ice-water and have enough free acid present to make the mass liquid enough so that when a drop of it is added to the beaker it soon dissolves leaving a fine white powder instead of sinking to the bottom as a hard lump, as it will do if too little acid is present.

The solution was filtered into a large beaker and heated to boiling. A boiling solution of oxalic acid (saturated in the cold) was added gradually to the solution with constant stirring, a large excess being used in order to make the precipitation complete in presence of so much sulphuric acid, and also to take any zirconium into solution; an excess can have no solvent effect whatever on the thorium present. The solution was allowed to stand and when cool, the white crystalline precipitate, the oxalates of thorium, cerium, lanthanum and didymium was

filtered and washed with a dilute solution of oxalic acid. It is better to allow the precipitate of the oxalates to stand many hours or if possible over night. The precipitate and paper were transferred to the precipitation beaker, 10–15 grams of stick potassium hydroxide added, 25–50 c.c. of water and the whole heated to boiling, washing down any oxalates that were attached to the sides of the beaker. The oxalates were soon changed to hydroxides having a silky appearance and becoming yellow on account of the oxidation of the cerium. The solution was diluted to about 300 c.c., filtered, and washed with water until free from alkali. The usual method was to dissolve the hydroxides in dilute hydrochloric acid and evaporate to dryness, but the evaporation of the chlorides is difficult, and often there is a separation of carbon due to incomplete washing of the hydroxides, which contain oxalates; this can be remedied by the addition of a little nitric acid, but the chlorides of the rare earths are difficult to obtain as neutral salts, due particularly to the syrupy nature of cerium chloride which is present in the largest quantity. The hydroxides were dissolved in hot dilute nitric acid (1:5) into the same beaker, the paper well washed with hot water and the solution of the nitrates evaporated to dryness on the water bath, moistened with water, and again evaporated until dry and neutral.

The nitrates were then dissolved in 200 c.c. of water and 25–50 c.c. of a saturated solution of sodium thiosulphate added, heated to boiling, filtered, washed, and the funnel and precipitate (precipitate A) set aside for subsequent filtration. The filtrate was precipitated with an excess of ammonia, filtered, washed and dissolved off the paper with hot dilute nitric acid (1:5) and evaporated to dryness, taken up with water and reprecipitated as before. This precipitate was filtered through the paper containing precipitate A and washed. All the thorium is precipitated by two precipitations, but is always contaminated with cerium, lanthanum and didymium.

The precipitate and paper were transfered to the precipitation beaker, 10-15 grams of stick potassium hydroxide added, 25-50 c.c. of water and heated to boiling, diluted to about 300 c.c., filtered and washed. The hydroxides were dissolved

off the paper with hot dilute nitric acid (1:5.) into the same beaker, the paper well washed with hot water, and the solution evaporated to dryness as before. The nitrates were dissolved in about 150 c.c. of water, heated to boiling and precipitated with a hot solution of oxalic acid, filtered, washed and either rinsed into the precipitation beaker with a saturated solution of ammonium oxalate, or the paper and precipitate placed in the beaker and about 200 c.c. of ammonium oxalate added. The beaker was heated on the water bath for an hour or so, stirred from time to time, diluted to about 350 c.c. and allowed to stand over night. The undissolved oxalates of cerium, lanthanum and didymium were filtered off, and the thorium precipitated in the filtrate with potassium hydroxide instead of ammonium hydroxide, since thorium hydroxide is soluble in hot ammonium oxalate. The thorium hydroxide was filtered off, washed, and dissolved in hot dilute nitric acid (1:5), the paper well washed and the solution evaporated to dryness as before. This was dissolved in about 100 c.c. of water, heated to boiling and precipitated with a hot solution of oxalic acid, filtered, ignited and weighed after treating for fifteen minutes in the blast lamp.

*Fumaric Acid Method.**

Two grams of the sand were decomposed, as in the previous method, and precipitated as oxalates. The oxalates were changed to hydroxides by potassium hydroxide, filtered, washed and dissolved in dilute nitric acid (1:5) and evaporated to dryness. The nitrates were taken up with 200 c.c. of 40% alcohol, then 50 c.c. of a saturated solution of fumaric acid in 40% alcohol added, and heated to boiling on the water bath, filtered while still hot through a long stem funnel, and washed with 40% alcohol. It is here that the objection to the method is encountered, the precipitate being gelatinous fills the pores of the filter paper and makes the filtration extremely slow, and the washing incomplete. The precipitate of thorium fumarate was dissolved in hot dilute nitric acid (1:5) instead of hydro-

* J. Am. C. S., xxiv, 1902, 901.

chloric, and instead of evaporating to dryness, which produces a compact residue incompletely soluble in water, the thorium and other contaminating earths were precipitated as hydroxides with an excess of potassium hydroxide, and the hydroxides filtered off, washed and dissolved in hot dilute nitric acid (1:5), evaporated to dryness, taken up with 40% alcohol, and precipitated with fumaric acid, as before; filtered, washed, ignited and weighed as thorium oxide. This modification eliminates any chance of the other earths being enclosed in the insoluble residue on evaporation, and also any possibility of the thorium oxide being contaminated by silica.

Metanitrobenzoic Acid Method.

Two grams of the sand were decomposed as before, the oxalates were precipitated with a large excess of oxalic acid in order to redissolve any zirconum which would be precipitated by the metanitrobenzoic acid, these were decomposed with potassium hydroxide, diluted, filtered, washed and dissolved into the precipitation beaker with hot dilute nitric acid (1:5). This solution of the nitrates was evaporated to dryness on the water bath, moistened with water, and evaporated until every trace of free nitric acid was driven off, since the precipitate is soluble in dilute nitric acid and as nitric acid is set free in the reaction,

$$Th(NO_3)_4 + 4C_6H_4NO_2COOH = Th(C_6H_4NO_2CO_2)_4 + 4HNO_3,$$

all free nitric acid must be removed from the nitrates.

The nitrates were dissolved in 500-600 c.c. of water and 150-250 c.c. of metanitrobenzoic acid solution added slowly with constant stirring, and heated on the water bath at 60-80°C. until the precipitate has all collected and settled to the bottom. It was then filtered, washed by decantation, using a 5% solution of the precipitant, then placed on the filter and washed with the same solution. The precipitate was dissolved by hot dilute nitric acid (1:5) into the precipitation beaker, the paper well washed with hot water and diluted to 600 c.c.; methyl orange was added until a decided red color was produced, then 25 c.c. of metanitrobenzoic acid. This was neutralized with dilute ammonia (1:10) until a pink tint was obtained. This is best

done by placing beside the beaker another containing the same volume and amounts of acid and indicator, also containing some white powder, such as pulverised quartz, and frequently stirred during the titration to give the same appearance as the contents of the other beaker. As the excess of nitric acid is neutralized the thorium reprecipitates as metanitrobenzoate, and when the nitric is neutralized the solution changes from a decided red to a pink color, due to the feeble acidity of metanitrobenzoic acid. After the pink tint was obtained 50 c.c. more of metanitrobenzoic acid were added to ensure complete precipitation. The beaker was then heated on the water bath to 60-80°C., the precipitate filtered, washed, and the wet precipitate ignited and weighed after treating for fifteen minutes with the blast lamp.

In the analysis of monazite some difficulty was experienced in always obtaining the resultant thorium oxide white, and also in the process of neutralization, for in making the second precipitation rapidly some experience is required to catch the proper end point. To obviate this the following modification was used, which, though a little longer, is much easier to carry out, and ensures concordant results and a pure white oxide.

After the first precipitate of thorium metanitrobenzoate was dissolved in nitric acid, instead of neutralizing with ammonia, the thorium is precipitated as hydroxide by potassium hydroxide. The potassium hydroxide at first causes a flocculent reprecipitation of the metanitrobenzoate, but a slight excess changes it to hydroxide; this is easily seen by the change from a very voluminous white precipitate to a more compact cream colored one. It was then diluted and filtered through the same paper, washed and dissolved with hot dilute nitric acid (1:5) into the same beaker, and evaporated to dryness, dissolved in 600 c.c. of water and precipitated with metanitrobenzoic acid, and the moist precipitate ignited, and the resultant thorium oxide weighed.

This modification is recommended, as it requires no experience with the use of the indicator, and if the preceding directions are carefully carried out a snow white oxide will always be obtained.

Results on Monazite Sands.

	Metanitrobenzoic.	Modified Metanitrobenzoic.	Fumaric.	Combination.
Refined Brazil Monazite.*	5.70 5.80 5.93	5.70 5.67 5.65 5.73 5.60	5.70	5.63
North Carolina Monazite.	5.48 5.12	5.27 5.26 5.27	5.13	5.39
Brazil Monazite.	4.89 4.97 5.04	4.99 4.98 4.82	4.85	4.90
High Grade North Carolina Monazite.†	6.04 6.15 5.88	6.02 6.04 ‡ 5.88 ‡ 6.15	5.89	5.98
Refined Brazil Monazite.*	---- ----	5.81 5.71	5.71	5.97

* It was through the kindness of Mr. Whitaker, of the Welsbach Light Co., that these samples were obtained.

† From the original sample received from Prof. Baskerville, not the same as used by Metzger. J. Am. C. Soc., xxiv, 1902, 901.

‡ The digestion for these two lasted three hours.

CONCLUSIONS.

1. Metanitrobenzoic acid precipitates thorium quantitatively as Th $(C_6H_4NO_2CO_2)_4$ from a neutral solution of the nitrate.

2. When this precipitation is repeated it affords a complete separation from cerium, lanthanum and didymium.

3. This method gives as good results for thorium in monazite as the combination or fumaric acid methods, and has the advantage in that it is much shorter, and offers no difficulties in precipitation or filtration; the precipitant is not expensive and avoids the use of alcohol.

BIOGRAPHICAL.

Arthur C. Neish entered Queen's University, Kingston, Ontario, in October, 1894, graduated in May, 1898, receiving the degree of A.B. in chemistry and animal biology. Remained one year longer, continuing the same work. In October, 1899, entered Columbia University holding the scholarship in chemistry, and received the degree of A.M. June, 1900. In June, 1900, he was appointed Assistant in Qualitative Analysis, Columbia University, and held the same until June, 1902. In October, 1902, pursued graduate work in chemistry for the degree of Ph.D., again holding the scholarship in chemistry. In February, 1903, was appointed Tutor in General Chemistry, Columbia University.